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Electrolytic Production of Metallic Calcium

ELECTROLYTIC PRODUCTION OF METALLIC CALCIUM

BY

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A. B. University of Illinois, 1916.

THESIS

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

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ENTITLED ELECTROLYTIC PRODUCTION OF METALLIC CALCIUM.

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

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June 1, 1917.

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INTRODUCTION.

Calcium was discovered in 1808 by Sir Davy and also by Berzelius. It has been a chemical curiosty of more value in museum than in laboratories. One gram of calcium once cost 17_s 6_d ($4.40), but now it is prepared at 9_s 7_d ($2.40) to 12_s ($3.00) per kilogram.

Bunsen first prepared it in the pure state in 1855, and Moissan obtained it later in the form of lustrous crystalline powder by heating calcium iodide to a dark red heat with an excess of sodium which also served to dissolve the metallic calcium as it was formed.

AS it is now being produced on a commercial scale at Bitterfield, Germany, and Holcomb Rock, Va. in this country. It seemed worth while to study its preparation with a view to ascertaining under what conditions it could conveniently be prepared in the laboratory.

OCCURRENCE OF CALCIUM IN THE NATURE.

Calcium compound is very abundant and widely diffused in nature, especially as calcium carbonates in the form of marble, chalk, calspar; as phosphate in phosphorite; as sulphates in gypsum ($CaSO_4$ $2H_2O$), anhydrite ($CaSO_4$) and alabaster in massive forms; as fluorite in fluospar (CaF_2); as a pure silicate in wollastonite ($CaSiO_3$), and with other metals in apatite, and also abundant as a component of various other rocks. It is found in all vegetables in small quantities and also in animal organisms, in egg shells, sea shells etc. It occurs also in extra-terrestial bodies in the Sun, meteorites, and many fixed stars.

CHEMICAL AND PHYSICAL PROPERTIES OF METALLIC CALCIUM.

Calcium is a silvery white metal, which melts at 760 degree C. It is soft enough to cut and is malleable, but less so than sodium and potassium. The fractured surface of calcium is more brilliant than that of steel, with a gray white color. When cut or filed it exhibits a yellowish tinge resembling German silver or gold alloyed with a great excess of silver. The globules of the metal may be nearly freed from chloride with absolute alcohol and ground on an emery wheel, then they become very bright. Its metallic luster is retained if it preserved in good petroleum. It may be turned into cylinders having a brilliant luster tarnishing in air. It may be drawn into wire of 0.5mm diameter. Its electric conductivity is 16, that of silver being 100.

It is relatively little affected when it is cold and dry by oxygen, hydrogen, chlorine, bromine, and iodine, all of

which react with the metal at a high temperature. In a current of air calcium units with both oxygen and nitrogen forming CaO and Ca_3N_2. With hydrogen it forms CaH_2 which is also prepared commercially by passing hydrogen into molten calcium. This compound with water generates a large amount of hydrogen. Calcium decomposes water in cold with enormous evolution of energy.

The metallic calcium is quite stable. The red hot molten metal can be stirred about in the furnace quite vigorously and even be dipped out and poured back without igniting. But once ignited it burns all with very intense blinding flame which resembles the flame of magnesium. When the hot metal is exposed directly to the air it changes rapidly to a white mass. If some of the metal is collected on a wire and struck smartly on the table, it will fly in all directions with a hissing sound and burns violently. Similar action takes place when the hot metal comes in contact with asbestos or with reducible substances.

Calcium, although soluble in molten sodium from which it separates in the crystalline state on solidification of the solvent, is not soluble in potassium. With magnesium it formes an alloy which decomposes cold water. With zinc and nickel it forms brilliant alloys. Tin heated just above its point of fusion, combines with it with incandescence, forming a white crystalline alloy containing 3.82% calcium.

EARLY INVESTIGATIONS ON PRODUCTION OF CALCIUM.

Lies-Bodart and Gobin[1] obtained the metallic calcium by heating the iodide with sodium in an iron crucible, the lid of which was screwed down. Moissan repeated this experiment several times ,and states that the yield and purity increased greatly, the richest metal obtained containing from 83to 93% of calcium, and that the reaction proceeds best at a dull red heat and is reversible if afterwards the temperature is raised to white heat.

Another process[2] consists in fusing 3 parts of $CaCl_2$ with 4 parts of zinc and 1 parts of sodium, thus forming an alloy of Zn and Ca which when heated in a gas carbon crucible, decomposes the Zn volatilizing and a button of fused Ca remains.

Moissan points out the defficulty of separation is to free the metallic calcium from the metal with which it becomes associated in the preparation and he succeeded in obtaining the pure metal by utilizing its property, unknown his resarch, of molten sodium to dissolve calcium, For preparation he modified the method of Lies-Bodart and Gobin. Moissan was probably the first to prepare the pure metal in large enough quantities to study its properties and behavior thoroughly. His method of recrystallizing the metal from solution of sodium was the best for preparing the pure metal until difficulties surrounding the electrolysis of molten calcium chloride had been overcome.

The production of calcium-amalgam and its subsequent distillation to obtain the free metal was studied by Davy, Berzelius and Pontin, Hare, and Bunsen. This seems to be the only way of preparing the metal from its acquous solution of its salts.

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[1] Compt Rend. 47, 23.

[2] Annalen 115, 3[illegible].

In 1854, Bunsen tried to obtain the metal by electrolyzing molten calcium chloride, but he was unsuccessful.

In 1856, Mathiessen[1] tried the same method and obtained rather impure metal. He used a mixture of the chlorides of calcium and strontium.

In 1890, Von Lengyol[2] obtained the metal of 99.2% purity by the same method using a porous earthenware diaphragm. Only a small quantities were obtained. He used 70-110 volts for 10-18 amperes.

In 1902, Borchers and Stockem,[3] Ruff and Plato,[4] and Arndt[5] prepared the metal on a large scale and with better apparatus. Ruff and Plato used a mixture of 100 parts of calcium chloride and 16.5 parts of fluoride which melts at 650 C. Borchers and Stockem obtained the metal in spongy form which was squeezed with a pair of tongues and remelted. The metal obtained by this way was proved to be impure, for the molten metal combines with nearly all the gases except those of helium group. There possibly exists considerable amount of oxide and hydride. If the temperature is kept high the molten metal will rise to the top of the bath and can be removed with a ladle.

In 1904, a great advance was made when the method of drawing out the calcium as a rod attached to the cathode was described.[6] THis seems to be the key to success and gives much better results than any other ways.

In the same year, Woehler describes the electrolysis of $CaCl_2$

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[1] J. Chem. Soc. 8, 27, 1856.
[2] J. Chem. Soc. 76, 218, 1899.
[3] J. Chem. Soc. 84, 19, 145, 1903. Ber. 36, 17-18, 1903
[4] J. Chem. Soc. 84, 10, 211, 1903., 86, 731, 1904.
[5] Zeit. Electrochem. 8, 861, 1902.
[6] U. S. Pat. 913,539., Chem.Centr. ii, 1180, 1904.

in an iron crucible, using an iron rod as cathode and a carbon anode, and he drew out a solid stick of calcium.[1]

In 1904, Moissan[2] showed that if a carbon cathode be used both calcium and carbide are obtained.

In 1906, Tucker and Whitney[3] improved the apparatus of J. H. Goodwin by water cooling the cathode and leaving a thin bottom of graphite between the electrolyte and the cooling coil. Fluorspar was placed on the bottom of the crucible and molten calcium chloride was poured over it. A current efficiency of 60% was obtained.

In 1908, Price and Harry[4] patented the use of an anode of Calcium carbide and in 1909, Cowper-Coles[5] patented the use of a disk cathode which revolves and removes the metal from the electrolyte.

Experiments done by Joseph H. Goodwin[6] at the University of Pennsylvania in 1903 and 1904 are noteworthy. The cathode of wrought iron is firmly fastened in electrical contact with a copper water-jacket which serves as a cooler and as base for the furnace. He used an Archeson graphite ring separated from the base by asbestos and made by boring out a 2.5 inch disk from a 6 inch graphite electrode. This ring constitutes the walls of the furnace and is also the anode. Its electrical connection is made by two wrought iron bands clamped firmly around it. When the furnace had been arranged, he spread powdered lime to the depth of half an inch over the bottom and melted it to form a

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1. J. Chem. Soc. 88,ii, 708, 1905.
2. J. Chem. Soc. [illegible],ii,483, 1904.
3. J. Am. Chem. Soc. 28, 84, 1906.
4. U. S. Pat. 886,857.
5. Brit. Pat. 24,396.
6. J. Am. Chem. Soc. 25, 873, 1903.

firm smooth floor. A stream of water was then sent through the jacket and the switch was closed. Anhydrous calcium chloride, fused for half an hour in a wind furnace was next poured into the furnace. It did not readily wet the graphite, it shrunk away from it; consequently a sheet of beautiful purple light separates the chloride from the graphite. It was an electric arc with a back electromotive force of 50 volts which lowers the current. He passed a current of 100 amperes and the temperature of the cell was kept at 950° C by pouring in calcium chloride from time to time.

The calcium liberated melted from the iron rod, upon which it had been deposited, and floated to the surface, forming a globule which was removed with a small sheet iron spoon when about an inch in diameter. The purity of the metal obtained in this manner varies with the purity of the chloride used. He found some magnesium and iron in his product.

F. C. Frary and W. L. Badger[1] worked on the preparation of calcium at the University of Minnesota in 1909. They tried the Borchers thpe of furnace, but often could not keep the melt fluid with the maximum current available (250 amperes), then they tried with the apparatus of Tucker and Whitney which is the form of Goodwin improved by water_cooled cathode, and found the following difficulties: (1) poor contact between the crucible and the copper strip clamped around it, (2) rapid destruction of the crucible due to oxidation, (3) the anode effect.

To remedy the first, they plated a layer of copper 1/16 to 3/32 inches in thickness upon the lower part of the crucible, and they found the increase of the efficiency. To protect the crucible they coated the upper part of the crucible with

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[1] Trans. Am.Electrochem. Soc. vol. 16, 1909.

carborundum fire sand and water glass, but this was unsuccessful for it cracked off when became hot. They also studied on the anode effect current efficiency which they stated as high as 100% in some runs.

A. R. Johnson[1] of the University of Wisconsin also studied and obtained the calcium by the same method as described for Frary. Some of the furnaces used by the early investigaters are shown in Fig. 1.

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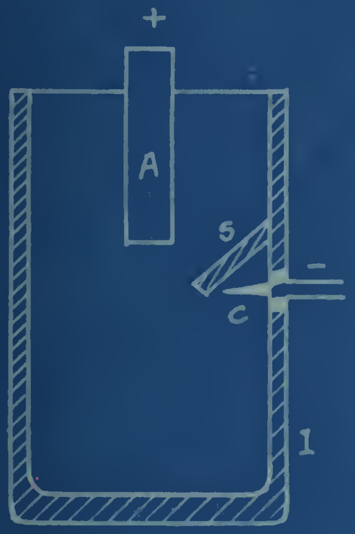
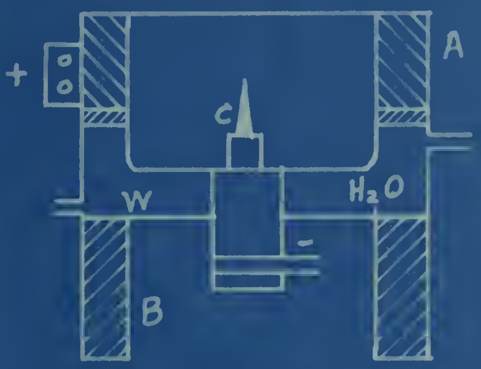
1. Trans. Electrochem. Soc. Vol. 18, 1910

Figure I.



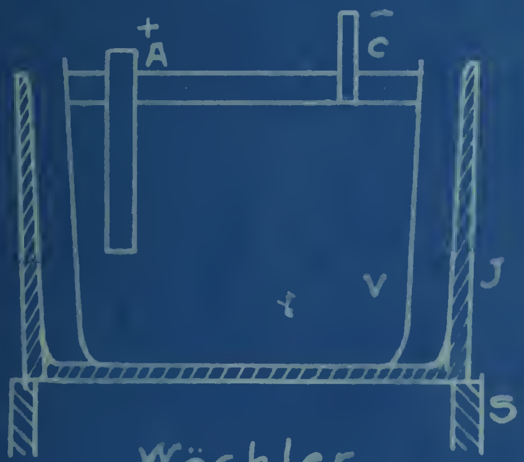
Borchers

A Carbon anode
C Iron needle cathode
I - Iron vessel.
S - Shelf.



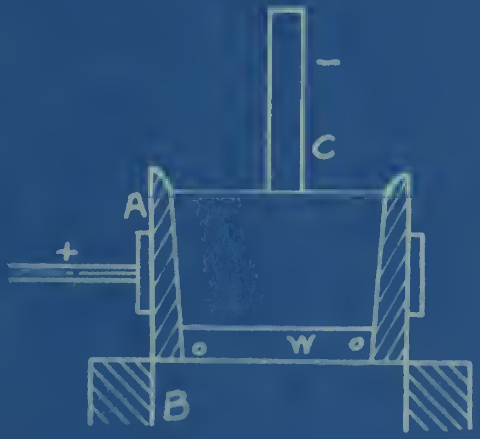
Borchers-Stockem

A - Graphite circular anode
C - Iron needle cathode
W - Water cooled bottom.
B - Brick support



Wöchler

A Graphite anode.
C - Iron cathode.
V - Iron vessel
J - Iron jacket
S - Support.



Goodwin.

C - Iron cathode.
A - Circular graphite anode.
W - Water cooled bottom
B Brick support

THE OBSERVATIONS.

EXPERIMENTAL PHENOMENA.

The apparatus of the Borchers type and Rathenau type are two different types for electrolyzing. The former uses high current density and consequently obtain the calcium in a molten condition , in which it rises to the surface and is skimmed off, while the latter type obtain the calcium in a compact form, that is, plated out at a moderately low current density.

Because of the successful results obtained by Goodwin, Frary, Woehler, and Johnson I also studied the electrolysis of calcium chloride with an apparatus of this type.

A considerable number of trials with apparatus were carried out, but by the poor apparatus and manipulation I could not obtain much calcium until the apparatus was improved.

A run was made using pure $CaCl_2$ in a cylindrical graphite vessel. It was melted from the inner surface by striking arcs using a carbon rod. When it was sufficiently hot the $CaCl_2$ gradually formed a small pool. When sufficient electrolyte was melted the iron cathode was lowered into the fused mass by means of a screw which was fastened rigidly to the iron stand, and then electrolysis began. After two or three minutes the odor of chlorine was noticed and there was numerous cracking and snapping at the vicinity of the cathode. Several yellow flames were also noticed. (The current of 100 to 120 amps. was flowing). After a few minutes the iron cathode was cautiously raised from the bath. Then suddenly an arc was struck at the end of the electrode and the surface of the bath. Again the electrode was lowered and electrolysis was continued. After three or four minutes the electrode was raised again slowly. An arc again

appeared and a bright beads of metallic calcium were observed on the surface. These beads were carefully removed with a spoon and cooled with a coat of $CaCl_2$. When the melted calcium was exposed to the air it changs to oxide (CaO) and nitride (Ca_3N_2) very rapidly and often it burns away with a blindly bright light. It also spatters away when it burns; so it is quite dangerous to handle. The current was gradually cut down to 60 to 70 amperes, (13 volts across the cell) which seems to be best suited for this process, and at which point an irregular deposit of metallic calcium at the end of the rod was noticed when the cathode rod was raised slowly. The current became less and less while electrolyzing and the deposit became smaller and smaller. Only a small space of molten salt was left between anode and cathode, and finally the current entirely ceased to flow.

The calcium deposit was taken away from the cathode by knocking it when it was cooled, and crashed the $CaCl_2$ off with a hammer. Then it was placed in absolute alcohol overnight in order to dissolve the chloride. Often it is necessary to boil in absolute alcohol to facilitate the removal of the $CaCl_2$.

The upper portion of the electrolyte changed its color to very dark after the electrolysis, while the inner part of it remained white after it has been cooled.

Woehler and others recommended to use a mixture of 100 parts of $CaCl_2$ and 17 parts of CaF_2 by weight for the bath, thus the electrolyte fuses at much lower temperature. This has been tried several times. When this mixture was used it melts easily and it is more liquid than $CaCl_2$ alone used. But it was found that the calcium obtained was not so good form as in

case of pure $CaCl_2$ alone used, it was difficult to get a long rod on the cathode, for it always tends to extend across the anode and melts off by striking an arc.

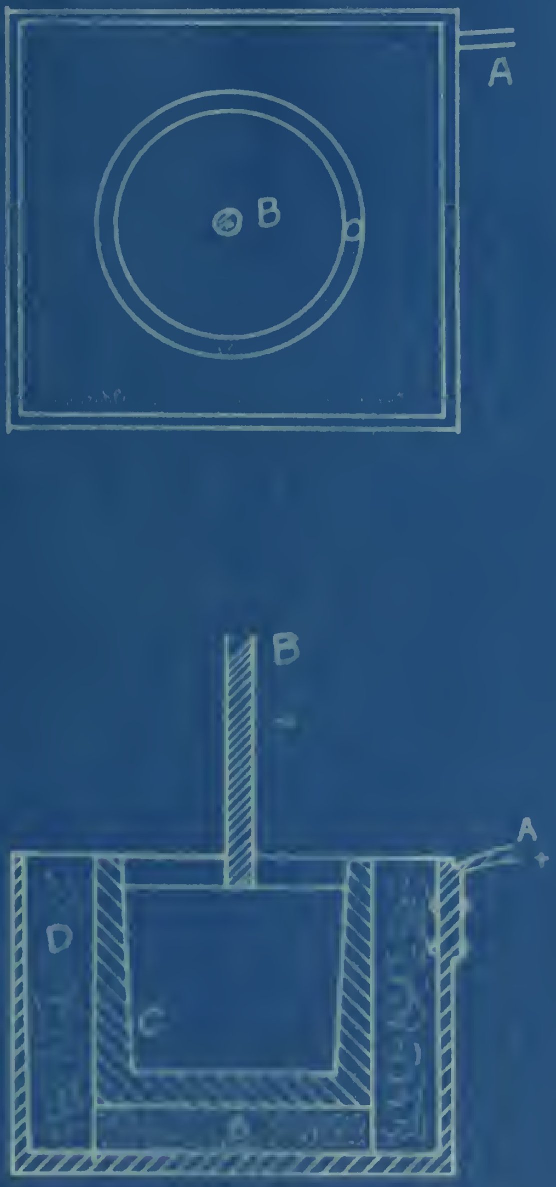
Difficulty was experienced in melting the solidified $CaCl_2$ again in the crucible. I tried to use alternating current resistance furnace to melt the $CaCl_2$ and poured it into an Acheson graphite crucible, but it was difficult to keep in liquid condition after it was poured, for it solidifies very quickly. So at last I tried to heat the crucible sufficiently to melt the salt with alternating current and electrolyzed with direct current, and I obtained a very good result. When the bath was cooled down again passed the alternating current to keep it in fused condition.

It was found that when the bath is too hot the iron rod becomes red hot and the calcium can not solidify on it, consequently it strikes an arc and floats away. On the other hand if the iron rod is cold the molten metal solidifies easily and a long rod of calcium can be obtained. For this reason the water-cooled cathode is advantageous.

The Fig. 2 shows the furnace which I used in this experiment.

Figure II.

Electric Furnace



A - Metallic conductor connecting anode vessel.

B - Iron cathode fastened to a stationary upright screw.

C - Archeson graphite anode.

D - Space filled with sand and cement.

S - Space filled with powdered carbon.

EXPERIMENTS WITH RESISTANCE FURNACE.

In order to keep the bath at a certain temperature, say 900°C, the electrolysis was conducted in an alternating current resistance furnace where the temperature can be kept constant by regulating the current. The crucible and the other apparatus were the same as before, the diagram of which is shown in Fig. 3.

First a run was made using pure $CaCl_2$. As the salt warmed up some steam and a little HCl came off, bubbling and spattering occasionally. The whole mass then came to a state of fusion at a very light cherry-red color. Too high temperature avoided by switching the alternating current off.

When the direct current was switched on using an iron cathode of about half an inch in diameter. Chlorine gas was immediately detected coming off and calcium was noticed at the cathode after a short time, yet it did not solidify on the cathode; it was floating round the bath in a molten condition. When the current was cut down to about 70 amperes and the electrode was cooled, the calcium began to adhere to the end of the rod, and it was gradually raised. A long rpd of metallic calcium coated with $CaCl_2$ was obtained.

When the bath was getting too cold the furnace was heated again and at the same time a little of CaF_2 was added and stirred. A little bluish color, as that of burning sulfur, was noticed on the surface. The bath was soon melted and CaF_2 was easily dissolved in the bath. The bath was more fluid and more limpid than before. The electrolysis was done as before, but it was rather difficult to obtain a very long rod of the metal in this case.

The $CaCl_2$ and CaF_2 used must be anhydrous. It may be done by heating them in an iron pan and in a crucible in the resistance furnace. The presence of water in electrolyte gives a poorer result even if it is very small amount. Much chlorine is not given off and calcium is not deposited so quickly as before even the temperature and current density are high enough for electrolysis, and finally a poor deposit is obtained.

In regard to the different diameters of the iron rod, it may be found that in case of using a rod of less than 1 cm the current density is too great for deposition of calcium at the end, while if a much larger rod were used the deposit is very crystalline and irregular and is mixed with much $CaCl_2$.

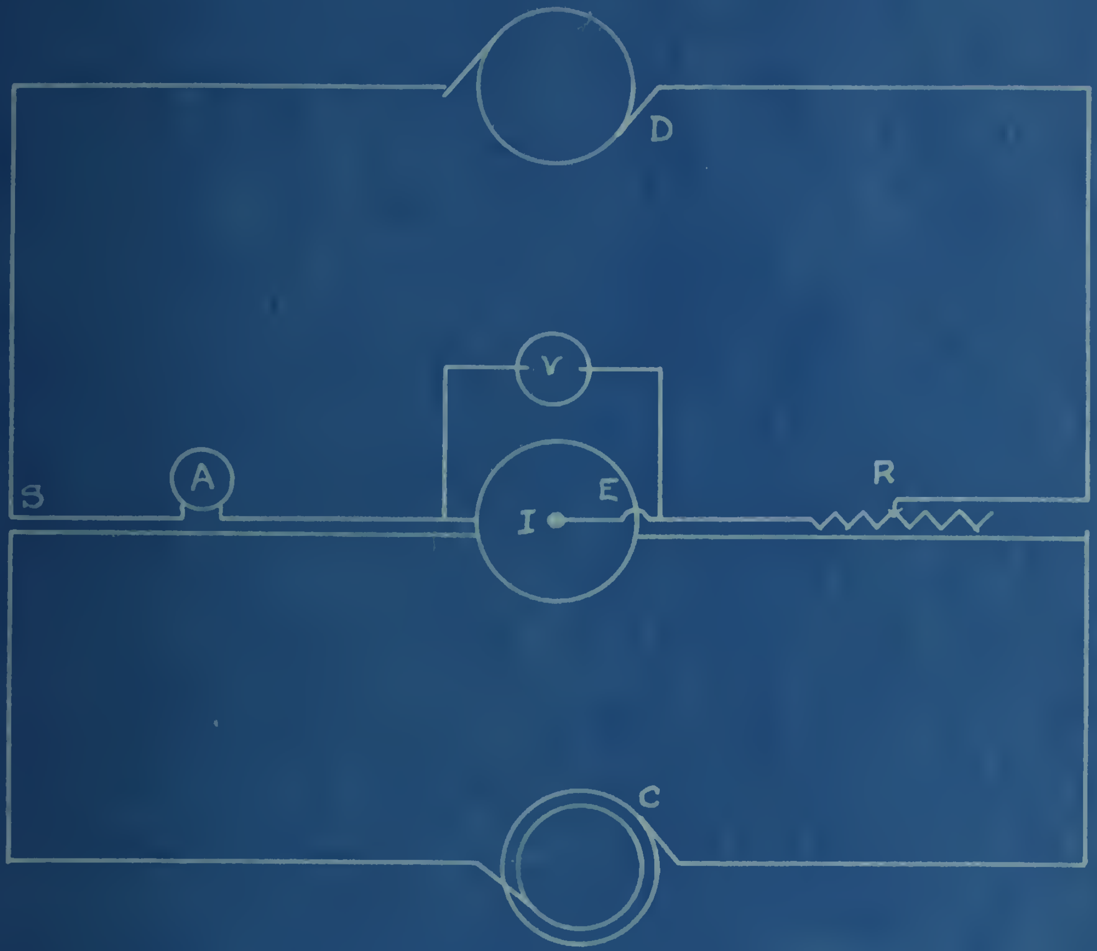
Cathode current density also has an important effect on the structure and nature of the deposit and also on current efficiency. But it is quite difficult to maintain a definite current density even for a short time, for it is changing all the time as the deposit grows. The deposit is irregular having different cross section at different parts.

Anode current density is not of so great importance as is cathode current density. Sufficient anode surface is only needed so that $CaCl_2$ can fuse as far as it likes with the given current in use.

The deposited calcium usually break off easily from the cathode owing to the difference in rate of contraction of the two metals. Yet often it does alloy with iron, especially when the iron is too hot, and it is impossible to remove all of the calcium from the rod.

Figure III.

Diagram of Connections



I - Iron cathode.
E - Electrolyzing vessel.
C - Alternater
D - Direct current dynamo.
R - Rheostat
A - Ammeter.
V - Voltmeter
S - Switch.

EXPERIMENTS WITH LARGER CATHODE RODS.

Finally an experiment was performed with a large water-cooled cathode. Two and half an inches was the diameter of the rod. It did not give a satisfactory result, although a large amount of current was passing. The metal separated was floating around the bath and did not deposit on the rod as in the case of smaller cathodes. After a few minutes run a coating of $CaCl_2$ intermixed with the metallic calcium was noticed on the cathode, when it was slowly and carefully raised. The metal obtained was impure and a small quantity. The coating of the mixture on the cathode came off easily and by crushing it the small lumps of the metal were separated. The current efficiency and current density were low.

Then a rod of one inch diameter was tried. Calcium rod could not obtain in this case as before, although a current of more than 200 amps. was passing.. The electrolyte was in good condition, and a large amount of calcium was separated in the bath. Whenever the cathode rod was raised an arc struck and the molten metal separated off. The is likely to be due to the too hot bath and cathode on which the metal could not solidify. The molten Ca was skimmed off with a spoon. The water-cooling apparatus did not work very well, because of the poor circulation of water in the cathode.

The rods used in this experiment are evidently too large for the anode surface used.

CURRENT EFFICIENCY.

Several runs for determination of current efficiency were made, for it is great importancefrom the engeneering standpoint.

Goodwin[1] determined the current efficiency for a run of several hours using pure $CaCl_2$. His highest efficiency was 21.5 to 41.9 percent.

Woehler,[2] on the other hand, used a mixture of 100 parts of $CaCl_2$ and 17 parts of CaF_2, electrolyzing every five minutes raising gradually the rod. The section was cut off and dissolved in a weak acid solution. The hydrogen collected and from this the amount of calcium was calculated. His efficiency was 82.9 percent.

Tucker and Whitney[3] improved the apparatus of Goodwin, and claim an efficiency of 60 percent, using pure $CaCL_2$ as electrolyte.

Frary and Badger[4] used a large crucible of Acheson graphite, having a water-cooled bottom, and serving as anode, and a water cooled iron cathode a little over an inch in diameter. The cathode was raised slowly by means of a screw mechanism. He passed a current of about 70 amperes (about 25 vplts across the cell),,and obtained from 45 to 100 percent efficiency average being 90 percent.

Johson[5] used a mixture of 100 parts of $CaCl_2$ and 10.5 parts of CaF_2 with the same type of apparatus of Frary, passing current of about 70 amperes. He obtained from 67.05 to 93.3 efficiency.

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1. J. Am. Chem. Soc. 27, 1403, 1905.
2. Z. Elektrochemie --- 11, 612, 1905.
3. J. Am. Chem. Soc. 23, 84, 1900.
4. Trans. Am. Electrochem. Soc. 16, 117, 1910.
5. Trans. Am. Electrochem. Soc. 18, 142, 1910.

The method which I used to determine the current efficiency was that of Goodwin and others, using a mixture of 100 parts of $CaCl_2$ and 17 parts of CaF_2 as electrolyte. $CaCl_2$ around the metal was completely broken off and was boiled in absolute alcohol to dissolve all of the chloride. Then it was dried over a flame and weighed.

My best results are as follows:

Run no.	Time min.	Amps.	Volts	Grams	Eff.percent
1	10	60	13	5.0	68.5
2	10	60	13	4.7	76.2
3	6	50	12	3.1	85.5
4	7	60	13	4.7	91.2
5	5	60	12	3.4	92.3

The amperage was taken every minute and the average was taken for calculation. It was very difficult to run for a long time with a certain amount of current, for the $CaCl_2$ solidifies with metallic calcium and it slows down the current. If the uniform temperature of the bath was kept much better results should have been obtained.

The low efficiency may be due mainly to the poor manupilation, that is, irregular raising of the cathode , and to the occasional feed of fresh electrolyte that effects the temperature of the bath. Too large current density also lowers the efficiency, for it gives spongy form of calcium deposit on the cathode rod.

CHEMICAL CHANGES IN ELECTROLYTE.

When $CaCl_2$ was heated steam came off first, then hydrochloric acid fume, then babbles of hydrogen appeared all over the bath. Yellow flames appeared lastly on the surface near the cathode. It may be the hydrogen that gives this flame.

Woeler states that H_2O remained after the temperature has reached a certain point begins to combine with $CaCl_2$ to form Cl-Ca-OH. This compound releases water with difficulty, and it probably react with metallic calcium to form anhydrous oxychloride and hydrogen during the electrolysis.

It is assumed by some chemists that there may be a reaction in the bath, $CaCl_2+Ca= 2CaCl$, forming thus a subchloride in high temperature, just as the case of the electrolysis of NcCl, and this may reduce the yield of the metal when the bath was too hot. But such a compound has never been prepared at any condition, and it is quite doubtful whether there is such a compound or not.

It is , howevr, probably true that some calcium is dissolved in $CaCl_2$ in high temperature. The black coloration in the chloride after the bath was cooled is not entirely due to carbon from the crucible, but it may possibly be a finely divided form of the calcium dissolved in it, for the most of metals are black when they are in finely divided form. The metallic calcium is much lighter than $CaCl_2$; so it stays at the surface, while the inside of the bath remains white after it was cooled, or it might be dissolved while it was hot, but it might crystallize out when the electrolyte became cooled.

I believe that there is not much chance for forming calcium carbide in the bath, for the temperature is not high enough for it, but a trace of calcium carbide may be found near the cathode

PRODUCTION AND APPLICATION OF METALLIC CALCIUM.

Calcium is produced commercially at Bitterfield, Germany, but nothing has been published as to its process, amount of production, commercial efficiency and its value.

It is made in the United States Of America by the Virginia Electrolytic Company at Holcomb Rock, Virginia. The process is to electrolyze melted calcium chloride in a cell patented by Seward and von Kuegelgen[1] and calcium is drawn off gradually with a hook, after it has been collected around a water-cooled collecting ring.

The production of calcium by this company in 1907 was 350 pounds, valued at $613, and about the same amount was produced in 1908[2].

Calcium is a good reducing agent, so it is frequently employed in some organic preparations, as in the Grignard reaction. It also employed commercially for removing the last trace of carbon from metals and alloys. The last trace of water in absolute alcohol will be removed with Ca filings. Since it combines with nearly all the gases except helium group very high vacuo can be obtained with calcium.

As stated before if hydrogen gas is passed through melted calcium it forms CaH_2 and this compound generates enormous amount of hydrogen with water, and this is employed in aeronautic purposes.

Calcium alloys with Al. Sb. Pb. Hg. Na. and Zn, and some very useful alloys can be obtained as in case of Ca and Pb which is made commercially. It is no doubt that Ca will be used many other useful ways in the future, and this remaines for investigation.

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[1] U. S. Patent 880,760. [2] Min. Ind. 17, 99, 1908.

CONCLUSION.

As stated before, if I used a water-cooled cathode of iron pipe with good circulation of water the yield would be much greater as Tucker and Whitney[1] recommended. Also the poor yield is due to poor manipulation, mostly to the rate of the withdrawal of the metallic rod from the electrolyte.

As to diameter of the cathode two to three cm seems to be the best, yet a smaller one may be used as well. If the rod is too large the metal will not deposit nicely. The main reason is to because the bath is too hot by the large current flowing.

There will be no short circuit if the metal is withdrawn at a proper rate using cold cathode surface, and thus a much better shaped metallic calcium rod will be obtained.

It is quite important to keep the bath at a constant temperature, that is above the melting point of calcium, say 800 C, in order to obtain a good result.

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1. J. Am. Chem. Soc. 28, 84, 1906.

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